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EXAMINER

LEE, CYNTHIA K

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**BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES**

Application Number: 09/997,604
Filing Date: November 29, 2001
Appellant(s): NEMOTO ET AL.

BURR & BROWN
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed 1/13/2006 appealing from the Office action mailed 6/28/2005.

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the brief.

(2) Related Appeals and Interferences

The examiner is not aware of any related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Claimed Subject Matter

Rejection of claims 12 and 19 under 35 USC 112, first paragraph has been withdrawn. Aside from the aforementioned withdrawal, the summary of claimed subject matter contained in the brief is correct.

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the brief is correct.

(8) Evidence Relied Upon

5700597	Zhong	12-1997
6106975	Watanabe	8-2000
5631104	Zhong	5-1997
5961949	Manev	10-1999
5686203	Idota	11-1997

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

1. Claims 11-14, 16-21, 23, and 24 are rejected under 35 U.S.C. 112, first paragraph, because the specification, while being enabling forming a positive electrode comprising $\text{Li}(\text{Ni}_{0.5}\text{Ti}_{0.5})_{0.15}\text{Mn}_{1.85}\text{O}_4$ as the positive electrode active material using Li_2CO_3 , MnO_2 , TiO_2 , and NiO as the raw starting materials, the positive electrode active material having a cubic spinel structure having primary particles of substantially octahedral shape constituted mainly by flat crystal faces wherein the primary particles include particles having at least one side of each flat crystal face of 1 micron or more, does not reasonably provide enablement for forming all positive electrode material comprising mainly Li and Mn that are formed from a raw material mixture comprising Li and Mn, the positive electrode material having a cubic spinel structure and primary particles of substantially octahedral shape constituted mainly by flat crystal faces wherein the primary particles include particles having at least one side of each flat crystal face of 1 micron or more. The specification does not enable any person skilled

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in the art to which it pertains, or with which it is most nearly connected, to make the invention commensurate in scope with these claims.

The claimed invention encompasses compounds that are outside the scope of the one working example and disclosure. Not only are the claims broad, it appears that the amount of direction, the number of working examples, and the breadth of claims are not commensurate in scope with the disclosure as originally filed. Hence undue experimentation would be required to determine what other compounds other than those disclosed by applicant can be used to make and practice applicant's invention as claimed.

With respect to enablement commensurate in scope with the claims, section 2164.08 of the MPEP states:

"The Federal Circuit has repeatedly held that 'the specification must teach those skilled in the art how to make and use the full scope of the claimed invention without undue experimentation'. In re Wright, 999 F.2d 1557, 1561, 27 USPQ2d 1510, 1513 (Fed. Cir. 1993)... The determination of the propriety of a rejection based upon the scope of a claim relative to the scope of the enablement involves two stages of inquiry. The first is to determine how broad the claim is with respect to the disclosure. The entire claim must be considered. The second inquiry is to determine if one skilled in the art is enabled to make and use the entire scope of the claimed invention without undue experimentation."

Factors to be considered when determining whether the claimed invention would require undue experimentation are given in MPEP 2164.01 (a). In re Wands, 858 F. 2d

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731, 737; 8 USPQ 2d 1400, 1404 (Fed. Cir. 1988). Only the relevant factors will be addressed for determining undue experimentation of the presently claimed invention.

The relevant factors are (A) the breadth of the claims; (B) the amount of direction provided by the inventor; (C) the existence of working examples, (D) the level of predictability in the art; and (E) the quantity of experimentation needed to make or used the invention based on the content of the disclosure.

Factor (A) Breadth of the claims:

No guidance is given in the specification for the innumerable possible embodiments encompassed by the claims of a positive electrode active material composed mainly of Li and Mn which has a cubic spinel structure and having primary particles having substantially octahedral shape constituted mainly by flat crystal faces where at least one side of each flat crystal face of length of 1 micron or more. The positive active material as recited in the claims encompasses compounds that are not lithium manganese oxide compounds disclosed in the instant specification. The specification is directed only to lithium manganese oxide positive electrode active materials and does not disclose how to make positive electrode active materials that are not lithium manganese oxide and composed mainly of Li and Mn with the properties recited in the claims.

Factor (B) The amount of direction provided by the inventor.

Applicant gives general guidance of the production of the positive electrode active material by firing a raw material mixture consisting of given proportions of salt and/or oxides of various elements, including Li, Mn, and as necessary substitution/addition elements, in an oxidizing atmosphere at 700 to 900 °C for 5 to 50 hours on page 7 of the substitute specification. Applicant also states on page 11 of the substitute specification that the morphology of the primary particles of positive electrode active material can be varied by varying the composition of the positive electrode active material even though the same synthesis conditions are employed. Applicant also only provides 1 working example and 2 comparative examples. The one working example is given on pages 9-10 of the substitute specification where commercial powders of Li_2CO_3 , MnO_2 , TiO_2 , NiO are mixed and then firing the resulting mixture in an oxidizing atmosphere at 800 °C for 24 hours to give primary particles having substantially octahedral shape. Comparative example 1 of the present specification is drawn to commercially available LiMn_2O_4 having primary particles of 0.2 microns in size and comparative example 2 of the present specification is drawn to a positive electrode active material obtained by mixing Li_2CO_3 , MnO_2 , and B_2O_3 to give a molar ratio of $\text{Li}:\text{Mn}:\text{B} = 1:2:0.03$ and then firing the resulting mixture in an oxidizing atmosphere at 800 °C for 24 hours to give a deformed and overall roundish octahedral shape where the flat crystal face of octahedron remained partially but the edges or apexes had a curved surface (see page 9 of substitute specification).

Hence, the general teaching and the examples in the specification do not give guidance on how to make positive electrode active materials having substantially

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octahedral shaped particles having the recited claimed dimensions that are not lithium manganese oxide, or specifically, $\text{Li}(\text{Ni}_{0.5}\text{Ti}_{0.5})_{0.15}\text{Mn}_{1.85}\text{O}_4$.

Factor (C) The existence of working examples:

As stated above, applicant's disclosure of 1 working example does not entitle applicant to claim all positive electrode active material containing Li and Mn having primary particles of substantially octahedral shape with the claimed dimensions.

MPEP 2164.03 states "[h]owever, in applications directed to inventions in arts where the results are unpredictable, the disclosure of a single species usually does not provide an adequate basis to support generic claims."

Factor (D) The level of predictability in the art:

Applicant states on page 11 of the substitute specification that the morphology of the primary particles of positive electrode active material can be varied by varying the composition of the positive electrode active material even though the same synthesis conditions are employed which can be demonstrated by comparing working example 1 with comparative example 2. Thus, there is a level of unpredictability in the art with respect to obtaining the claimed morphology of the primary particles of the positive electrode active material.

With respect to the relationship of predictability of the art and the enablement requirement, MPEP 2164.03 states:

"The amount of guidance or direction needed to enable the invention is inversely related to the amount of knowledge in the state of the art as well as the predictability in the art. In re Fisher, 427 F.2d 833, 839, 166 USPQ 18, 24 (CCPA 1970). The "amount of guidance or direction" refers to that information in the application, as originally filed, that teaches exactly how to make or use the invention. The more that is known in the prior art about the nature of the invention, how to make, and how to use the invention, and the more predictable the art is, the less information needs to be explicitly stated in the specification. In contrast, if little is known in the prior art about the nature of the invention and the art is unpredictable, the specification would need more detail as to how to make and use the invention in order to be enabling. >See, e.g., Chiron Corp. v. Genentech Inc., 363 F.3d 1247, 1254, 70 USPQ2d 1321, 1326 (Fed. Cir. 2004)... The "predictability or lack thereof" in the art refers to the ability of one skilled in the art to extrapolate the disclosed or known results to the claimed invention. If one skilled in the art can readily anticipate the effect of a change within the subject matter to which the claimed invention pertains, then there is predictability in the art. On the other hand, if one skilled in the art cannot readily anticipate the effect of a change within the subject matter to which that claimed invention pertains, then there is lack of predictability in the art. Accordingly, what is known in the art provides evidence as to the question of predictability... However, in applications directed to inventions in arts where the results are unpredictable, the disclosure of a single species usually does not provide an adequate basis to support generic claims. In re Soll, 97 F.2d 623, 624, 38 USPQ 189, 191 (CCPA 1938). In cases involving unpredictable factors, such as most chemical reactions and physiological activity, more may be required. In re Fisher, 427 F.2d 833, 839, 166 USPQ 18, 24 (CCPA 1970)[emphasis added]."

Factor (E) the quantity of experimentation needed to make or used the invention based on the content of the disclosure.

This factor has been addressed by factors (A)-(C) above.

Thus, the claims are properly rejected for scope of enablement since the two stages of inquiry as set forth in MPEP section 2164.08 have been fully addressed herein by the Examiner.

Claim Rejections - 35 USC § 103

2. Claims 11-14, 16-21, 23 and 24 are rejected under 35 U.S.C. 103(a) as being unpatentable over the JPO machine translation of JP 08-217452 A in view of Zhong et al. (US Pat. No. 5,700,597, hereinafter '597) and Watanabe et al. (US Patent No. 6,106,975).

The JPO Machine translation of JP 08-217452 A discloses a method of manufacturing a lithium battery comprising the steps forming an electrode body by placing a positive electrode and a negative electrode in contact with a separator, the separator being positioned between the positive and the negative electrode so that the positive electrode is not in contact with the negative electrode (see Figure 1 and paragraph 81 of machine translation).

The JPO Machine translation of the reference also discloses that the positive electrode comprises a positive electrode active material which is composed mainly of Li

and Mn where the Li/Mn ratio is larger than 0.5 and positive electrode active material has a cubic spinel structure (see paragraph 34 of machine translation) and primary particles mostly have a substantially octahedral shape constituted mainly by flat crystal faces (see Figure 4 and paragraphs 76 and 107) where the length of one side of the octahedron is 1 micron or more. The positive electrode contains acetylene black as an electric conduction agent (see paragraph 108 of machine translation).

The primary particle size of the positive electrode active material can also be from 1 to 10 microns (see paragraph 56 of machine translation). Furthermore, since the positive electrode active material has the same particle shape, composition, and primary particle size as those disclose in the specification and being claimed in the instant claims, the primary particles inherently include particles having at least one side of each flat crystal face of length of 1 micron or more. The electrostatics and size of the primary particles inherently determine the size of the secondary particles and since the primary particle size range of 1 to 10 microns of JP 08-217452 A (see above) falls within the claimed range, the primary particles of JP inherently form secondary particles having a maximum particle diameter of 50 microns or less.

The positive electrode active material is formed of a raw material mixture comprising positive electrode precursor material comprising Li and Mn and heating the raw material mixture to a temperature and for a time which is effective to convert the raw material mixture into a positive electrode active material having the cubic spinel structure and primary particles having substantially octahedral shape (see paragraph 75 of machine translation).

The court has held that claiming of a property or characteristic which is inherently present in the prior art does not necessarily make the claim patentable. *In re Best*, 562 F.2d 1252, 1254, 195 USPQ 430, 433 (CCPA 1977). See also MPEP 2112 and 2112.01. When the Examiner has provided a sound basis for believing that the products of the applicant and the prior art are the same, the burden of proof is shifted to the applicant to prove that the product shown in the prior art does not possess the characteristics of the claimed product. *In re Spada*, 911 F.2d 705, 709, 15 USPQ2d 1655, 1658 (Fed. Cir. 1990).

The JPO machine translation of JP 08-217452 A does not disclose welding a plurality of current collecting portions directly to the positive electrode and to the negative electrode and that the battery has a capacity of 2Ah, and that the battery is used in an electric vehicle or a hybrid electric vehicle.

Zhong et al. '597 teach a lithium battery as a high energy density source for an electric vehicle (col. 1, lines 20-25).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use the lithium secondary battery in the electric vehicle because a lithium secondary battery has high energy density, is light weight, and would not cause exhaust air polluting substances during the operation of the electric vehicle.

It would have also been obvious to one of ordinary skill in the art at the time the invention was made to produce a lithium secondary battery having a capacity of 2Ah or more in order to operate a high energy consuming electronic device such as an electric vehicle since the power requirements of electronic devices differ and it would have been

obvious to manufacture lithium batteries with varying capacities for different applications. A person of ordinary skill in the art would be motivated to and would be knowledgeable about how to scale up the amount of active material necessary in a lithium secondary battery in order to provide enough electricity to operate an electric vehicle or any other electronic device.

Watanabe et al. teach ultrasonically welding a plurality of tabs (current collecting portions) directly to the positive electrode and to the negative electrode so that discharge and recharge takes place entirely without loss and evenly in a large size battery (col. 1, lines 45-60 and col. 9, lines 1-14).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to ultrasonically weld a plurality of tabs directly to the positive electrode and to the negative electrode so that discharge and recharge takes place entirely without loss and evenly in a large size battery such as battery having a capacity of 2Ah or more.

3. Claims 11-14, 16-21, and 23 are rejected under 35 U.S.C. 103(a) as being unpatentable over Zhong et al. (US Pat. No. 5,631,104) in view of Zhong et al. (US Pat. No. 5,700,597, hereinafter '597) and Watanabe et al. (US Patent No. 6,106,975).

Applicants' claims are directed to a method of manufacturing a lithium secondary battery comprising a positive electrode active material which is composed mainly of Li and Mn and has a cubic spinel structure and the primary particles of the positive

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electrode active material has a substantially octahedral shape constituted mainly by flat crystal faces.

Applicants disclose in the specification that the definition of "mainly composed of Li and Mn" means that part of the Mn in the lithium manganese oxide LiMn_2O_4 may be replaced by other elements such as an element selected from the group consisting of Li, Fe, Mn, Ni, Mg, Zn, B, Al, Co, Cr, Si, Ti, Sn, P, V, Sb, Nb, Ta, Mo, and W or that the lithium manganese oxide may contain B, Mo or W as an additive (see page 6, lines 18-25 to page 7, lines 5-10 of the specification). The applicants also prefer lithium manganese oxide to have a Li/Mn molar ratio of greater than 0.5 and examples include $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$ where Mn is partly replaced by Li, and $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ wherein Mn is partially replaced by M that is a substitution element other than Li (see page 7, lines 11-23 of the specification). Applicants also disclose on page 11, lines 5-10 that production of the positive electrode active material of the present invention is conducted by firing a raw mixture consisting of given proportions of salts and/or oxides of various element including Li, Mn, and as necessary, a substitution element and addition elements in an oxidizing atmosphere at 700 to 900 °C for 5 to 50 hours.

Zhong et al. disclose a lithium secondary battery comprising a positive electrode active material with the formula $\text{LiNi}_z\text{Mn}_{2-z}\text{O}_4$ where z can be 0.05, 0.1, 0.2, 0.3, and 0.5 (col. 8, lines 11-25) and Ni is the substitution element. The battery comprises an electrode group formed by placing a positive electrode and a negative electrode in contact with the separator, the separator being positioned between the positive electrode and the negative electrode so that the positive electrode is not in contact with

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the negative electrode (col. 6, lines 22-27 and Figure 1). The positive electrode also contains carbon black as a conductive agent (col. 7, lines 45-50).

The positive electrode active material was synthesized with LiMnO_2 , NiNO_3 , and LiOH powders in appropriate amounts and heat treated at $750\text{ }^\circ\text{C}$ in air for 4 hours and then the product was ground and mixed again followed by a second similar heat treatment for an additional 12 hours for z less than or equal to 0.3 (col. 8, lines 10-25). For the sample with z equal to 0.5, the first heat treatment lasted 16 hours and the second heat treatment was performed at $850\text{ }^\circ\text{C}$ for 12 hours. Zhong et al. also disclose in general that the heating can be performed between about 750 and $900\text{ }^\circ\text{C}$ and more than one mixing and heating step may be desirable (col. 4, lines 7-17).

Zhong et al. also disclose $\text{LiCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as the positive electrode active material synthesized using an appropriate mixture of EMD, Cr_2O_3 , and LiOH powders wherein the mixture was heat treated in air at $800\text{ }^\circ\text{C}$ for 4 hours, ground, remixed, and heat treated again at $900\text{ }^\circ\text{C}$ for 11 hours (applies to claim 10, col. 9, lines 32-37).

Zhong et al. also disclose $\text{Li}_{x+y}\text{M}_z\text{Mn}_{2-y-z}\text{O}_4$ as the positive electrode active material where the crystal structure is spinel and M is a transition metal, $0 \leq x < 1$, $0 \leq y < 0.33$, and $0 < z < 1$ (see abstract). The positive electrode active material is prepared by mixing reactant powders comprising electrolytic manganese dioxide, a transition metal source, and a lithium source in a stoichiometric manner followed by heating the mixture in an oxygen containing atmosphere from 750 - $900\text{ }^\circ\text{C}$ (col. 4, lines 4-17).

Since Zhong et al. disclose identical synthesis conditions and formulas for the positive electrode active material in the lithium battery as discussed above [Zhong et al.'s formula (see abstract) encompasses the formulas $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{Li}(\text{Li}_x\text{Mn}_{2-x})\text{O}_4$] as those of the applicants, the properties cited in the instant claims 11-14 and 17-21 are inherent in the positive electrode active material of Zhong et al.

The court has held that claiming of a property or characteristic which is inherently present in the prior art does not necessarily make the claim patentable. *In re Best*, 562 F.2d 1252, 1254, 195 USPQ 430, 433 (CCPA 1977). See also MPEP 2112 and 2112.01. When the Examiner has provided a sound basis for believing that the products of the applicant and the prior art are the same, the burden of proof is shifted to the applicant to prove that the product shown in the prior art does not possess the characteristics of the claimed product. *In re Spada*, 911 F.2d 705, 709, 15 USPQ2d 1655, 1658 (Fed. Cir. 1990).

Zhong et al. (US Pat. No. 5,631,104) does not disclose welding a plurality of current collecting portions directly to the positive electrode and to the negative electrode and that the battery has a capacity of 2Ah, and that the battery is used in an electric vehicle or a hybrid electric vehicle.

Zhong et al. '597 teach a lithium battery as a high energy density source for an electric vehicle (col. 1, lines 20-25).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use the lithium secondary battery in the electric vehicle because

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a lithium secondary battery has high energy density, is light weight, and would not cause exhaust air polluting substances during the operation of the electric vehicle.

It would have also been obvious to one of ordinary skill in the art at the time the invention was made to produce a lithium secondary battery having a capacity of 2Ah or more in order to operate a high energy consuming electronic device such as an electric vehicle since the power requirements of electronic devices differ and it would have been obvious to manufacture lithium batteries with varying capacities for different applications. A person of ordinary skill in the art would be motivated to and would be knowledgeable about how to scale up the amount of active material necessary in a lithium secondary battery in order to provide enough electricity to operate an electric vehicle or any other electronic device.

Watanabe et al. teach ultrasonically welding a plurality of tabs (current collecting portions) directly to the positive electrode and to the negative electrode so that discharge and recharge takes place entirely without loss and evenly in a large size battery (col. 1, lines 45-60 and col. 9, lines 1-14).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to ultrasonically weld a plurality of tabs directly to the positive electrode and to the negative electrode so that discharge and recharge takes place entirely without loss and evenly in a large size battery such as battery having a capacity of 2Ah or more.

4. Claims 11-14, 16-21, and 23 are rejected under 35 U.S.C. 103(a) as being unpatentable over Manev et al. (US Pat. No. 5,961,949) in view of Zhong et al. (US Pat. No. 5,700,597, hereinafter '597) and Watanabe et al. (US Patent No. 6,106,975).

Manev et al. disclose a lithium secondary battery comprising a positive electrode active material with the formula $\text{Li}_{1.025}\text{Mn}_{1.975}\text{O}_4$ having spinel structure and a mean particle size distribution of 2 microns (see col. 6, lines 5-10). The positive electrode active material was synthesized by heating 500g of ground MnO_2 and LiOH (raw material comprising Li and Mn) at a molar ratio of $2\text{Li}:\text{Mn} = 1.05$ and the mixture was fired at 750°C for 48 hours (col. 6, lines 1-5). Manev et al. also disclose that the mixture is generally fired in the presence of a gas flow such as air or a gas mixture containing from 5 to 100 percent oxygen by volume, which is an oxidizing atmosphere (col. 4, lines 45-48). A lithium secondary battery also inherently comprises an electrode body formed by placing a positive electrode and a negative electrode in contact with the separator, the separator inherently being positioned between the positive electrode and the negative electrode so that the positive electrode is not in contact with the negative electrode so that a short-circuit does not occur and enable the battery to function. Manev et al. also disclose that the positive electrode contains a conductive agent such as carbon black (col. 5, lines 45-50).

Since Manev et al. disclose identical synthesis conditions and formula for the positive electrode active material in the lithium battery as those of the applicants as discussed above, the properties cited in the instant claims 11-14 and 17-21 are inherent in the positive electrode active material of Manev et al.

The court has held that claiming of a property or characteristic which is inherently present in the prior art does not necessarily make the claim patentable. *In re Best*, 562 F.2d 1252, 1254, 195 USPQ 430, 433 (CCPA 1977). See also MPEP 2112 and 2112.01. When the Examiner has provided a sound basis for believing that the products of the applicant and the prior art are the same, the burden of proof is shifted to the applicant to prove that the product shown in the prior art does not possess the characteristics of the claimed product. *In re Spada*, 911 F.2d 705, 709, 15 USPQ2d 1655, 1658 (Fed. Cir. 1990).

Manev et al. does not disclose welding a plurality of current collecting portions directly to the positive electrode and to the negative electrode and that the battery has a capacity of 2Ah, and that the battery is used in an electric vehicle or a hybrid electric vehicle.

Zhong et al. '597 teach a lithium battery as a high energy density source for an electric vehicle (col. 1, lines 20-25).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use the lithium secondary battery in the electric vehicle because a lithium secondary battery has high energy density, is light weight, and would not cause exhaust air polluting substances during the operation of the electric vehicle.

It would have also been obvious to one of ordinary skill in the art at the time the invention was made to produce a lithium secondary battery having a capacity of 2Ah or more in order to operate a high energy consuming electronic device such as an electric vehicle since the power requirements of electronic devices differ and it would have been

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obvious to manufacture lithium batteries with varying capacities for different applications. A person of ordinary skill in the art would be motivated to and would be knowledgeable about how to scale up the amount of active material necessary in a lithium secondary battery in order to provide enough electricity to operate an electric vehicle or any other electronic device.

Watanabe et al. teach ultrasonically welding a plurality of tabs (current collecting portions) directly to the positive electrode and to the negative electrode so that discharge and recharge takes place entirely without loss and evenly in a large size battery (col. 1, lines 45-60 and col. 9, lines 1-14).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to ultrasonically weld a plurality of tabs directly to the positive electrode and to the negative electrode so that discharge and recharge takes place entirely without loss and evenly in a large size battery such as battery having a capacity of 2Ah or more.

5. Claim 24 is rejected under 35 U.S.C. 103(a) as being unpatentable over Zhong et al. (US Pat. No. 5,631,104) in view of Zhong et al. (US Pat. No. 5,700,597, hereinafter '597) and Watanabe et al. (US Patent No. 6,106,975) as applied to claim 17 above and further in view of Idota et al. (US Pat. No. 5,686,203).

Zhong et al. ('104) as modified by Zhong et al. ('597) and Watanabe et al. teach all the limitations of claim 24 except that the positive electrode further comprises

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acetylene black. It is noted that Zhong et al. ('104) disclose the positive electrode contains carbon black as a conductive agent (col. 7, lines 45-50).

Idota et al. teach a positive electrode comprising lithium manganese oxide (col. 8, lines 35-49) as the active material, that the positive electrode can comprise a conductivity imparting agent (col. 3, lines 1-7) and that the conductivity imparting agent may be carbon black or acetylene black and that the use of acetylene black is preferred because the resulting battery has high charge and discharge capacities (col. 13, lines 29-35).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use acetylene black instead of carbon black as the conductive agent in the positive electrode of Zhong et al. ('104) because the use of acetylene black results in a battery that has high charge and discharge capacities.

6. Claim 24 is rejected under 35 U.S.C. 103(a) as being unpatentable over Manev et al. (US Pat. No. 5,961,949) in view of Zhong et al. (US Pat. No. 5,700,597, hereinafter '597) and Watanabe et al. (US Patent No. 6,106,975) as applied to claim 17 above and further in view of Idota et al. (US Pat. No. 5,686,203).

Manev et al. as modified by Zhong et al. ('597) and Watanabe et al. teach all the limitations of claim 24 except that the positive electrode further comprises acetylene black. It is noted that Manev et al. also disclose that the positive electrode contains a conductive agent such as carbon black (col. 5, lines 45-50).

Idota et al. teach a positive electrode comprising lithium manganese oxide (col. 8, lines 35-49) as the active material, that the positive electrode can comprising a conductivity imparting agent (col. 3, lines 1-7) and that the conductivity imparting agent may be carbon black or acetylene black and that the use of acetylene black is preferred because the resulting battery has high charge and discharge capacities (col. 13, lines 29-35).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use acetylene black instead of carbon black as the conductive agent in the positive electrode of Manev et al. because the use of acetylene black results in a battery that has high charge and discharge capacities.

(10) Response to Argument

Response to arguments to Issue 2, rejection of claims 11-14, 16-21, 23, and 24 under 35 USC 112, first paragraph

Applicant argues that the USPTO is doubting the truth or accuracy of the disclosure (pg 10).

The Examiner notes that the scope of enablement of the claims follows two stages of inquiry set forth in MPEP 2164.08 and the objective truth of the statements that the invention would be useful is irrelevant and has nothing to do with scope of enablement of the claims rejected under 35 USC 112 first paragraph. The two stages of inquiry set forth in MPEP 2164.08 are to first determine how broad the claim is with respect to the disclosure and the second inquiry is to determine if one skilled in the art is

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enabled to make and use the entire scope of the claimed invention without undue experimentation. The Examiner has completed the two stages of inquiry above in the Grounds of Rejection.

Applicant argues that a skilled artisan would change the raw materials, temperature, and or duration of the process to provide a positive material and in view of the disclosure, pg. 11, lines 5-17 and page 12, lines 6-12, and page 14, lines 10-14, a skilled artisan might try heating the same raw materials to a lower temperature of heat for a shorter period of time.

The Office notes that if the Comparative Example, which was produced at the same temperature and duration as Example 1, did not produce the crystalline structures as claimed in claim 13, one of ordinary skill in the art would need more guidance that would lead to producing the same crystalline structure than a mere disclosure of "... firing a raw material mixture ... in a oxidizing atmosphere at 700 to 900°C for 5 to 50 hours" (pg 11 of the original specification) and "lowering the synthesis temperature and/or shortening the synthesis time" (pg 12 of the specification), and thus, undue experimentation would be necessary to determine the optimal temperature and time. Not only undue experimentation, but it would be based on a "trial and error" analysis to see which temperature and time would produce the octahedral crystalline structure.

Applicant cites that in In re Fuetterer 138 USPQ 217 that the CCPA held that there is no requirement that an applicant discover which of all the salts within the generic expression in the claim would function properly in the invention.

In response, the *In re Fuetterer* case is not an analogous situation to the presently claimed invention which specifically claims feature of a compound by what it is and not what it does, that is, the compound is not claimed functionally as was the situation in *In re Fuetterer*.

Comment: It is important to point out that applicant admits on pages 15-16 of the amendment filed on 1/4/2005 that processing positive electrode active material in the manner described in the present specification on page 11, lines 5-10 does not inherently result in the production of the positive electrode active material having the characteristic recited in the present claims:

... the process conditions employed in Comparative Examples 1 and 2 were *identical* (emphasis added) to those employed in the Example (differing starting materials were employed) and the Comparative Examples *did not* (emphasis in original) achieve primary particles having substantially octahedral shape, whereas the Example *did* (emphasis in original) achieve such primary particles.

This admission indicates that practicing applicant's invention is unpredictable.

Response to arguments to Issue 3, rejection of claims 11-14, 16-21, 23, and 24 under 35 USC 103(a), over JP 08-217452 (JP '452) in view of Zhong (US5700597) and Watanabe (US 6106975).

Applicant argues that JP '452 disclosure of "needle-like octahedral" structure does not read on applicant's "substantially octahedral" structure.

The Examiner gives the term "octahedron" in the reference and in the instant claim its plain, ordinary, and customary meaning complemented by applicant's definition of "substantially octahedral" in the substitute specification on page 6. As stated previously, the definition of a regular octahedron is an octahedron with eight equilateral triangles as faces (see Definition of Regular Octahedron [online]. Hyperdictionary, copyright 2000-2003 [retrieved on 2003-08-29]. Retrieved from the Internet : <URL: <http://www.hyperdictionary.com/dictionary/regular+octahedron>>). (The printout is attached.) Figures of a Six-Fold Regular Octahedron are also included in the previous Office Action which show eight equilateral triangular faces for the regular octahedron (Six-Fold Regular Octahedron [online]. Tomoko Fuse, 2002 [retrieved on 2003-08-29]. Retrieved from the Internet : <URL: <http://gallery.origami.free.fr/Auteurs/Japan/fuse/gallery/Six-Fold%20Regular%20Octahedron.htm>>). (The printout is attached.)

Applicant argues that the needle-like regular octahedron shapes disclosed in JP '452 do not fall within the definitions of "substantially octahedral shape" contained in the present specification (pg. 13-16).

The Examiner notes that claims are interpreted in the light of the specification. Although the definition of "substantially octahedral shape" is found in the specification, they were not claimed explicitly. A reading of the specification provides no evidence to

indication that these limitations must be imported into the claims to give meaning to disputed terms. *Constant v. Advanced Micro-Devices Inc.*, 7 USPQ2d 1064.

Furthermore, page 6 of the substitute specification defines the term “substantially octahedral” broadly to be the following:

“ The primary particles seen in Fig. 1 also include particles of other shapes, that is, a) particles wherein the apex formed by intersection of four crystal faces of octahedron is not complete and is formed in the form of a plane or an edge, (b) particles wherein a different crystal face is formed at the edge formed by intersection of two crystal faces of octahedron, and (c) particles wherein one crystal face is jointly owned by two primary particles or wherein other primary particles grows from the surface of of one primary particle. These primary particles do not have a completely octahedral shape but can be regarded as a substantially octahedral shape. In the present invention, the “substantially octahedral shape” include these various shapes and further include those polyhedrons formed by partial chipping of the above shapes or by joint possession of crystal face in complicated manners between two primary particles.”

Based on this broad definition for “substantially octahedral” in the specification, the regular octahedron needle-like particles of the reference can clearly be considered “substantially octahedral”.

Applicant argues that Fig. 3 and 4 of JP '452 do not show particles that are regular octahedral (pg. 14).

The Examiner notes that the applicants are not claiming a “regular octahedral” shape, but a “substantially octahedral” shape. The applicant has not provided any hard evidence, such as experimental evidence, that the crystals in the JP '452 reference are

not substantially similar, if not identical to those of applicant's invention as shown in Figure 1 of the instant application.

Applicant argues that there is not motivation to combine JP '452 with Zhong '597 and Watanabe '975 (pg. 17).

The motivation has been clearly addressed in the Office Action mailed on 6/28/2005 and is reiterated in the Grounds of Rejection above.

Comment: Applicant's assertion that the welding of plurality of current collecting portions directly to the electrodes contributes to the reduction of internal resistance according to the present invention is not supported by the original disclosure. The original disclosure does not state that welding the plurality of current collecting portions is the inventive feature to reduce resistance in the battery.

Response to arguments to Issue 4, rejection of claims 11-14, 16-21, 23 under 35 USC 103(a), over Zhong (US 5631104) in view of Zhong (US 5700597) and Watanabe (US 6106975).

Applicant asserts that the conditions and formulas in the methods of Zhong et al. ('104) are not identical to those of the present invention and would not produce primary particles having substantially octahedral shape and that the present specification at

page 11, lines 5-10 do not inherently result in production of positive electrode active materials having the characteristics recited in the present claim.

In response, the applicant has not disproven the Examiner's inherency arguments of the Zhong et al. ('104) reference because the specification states at page 11, lines 5-10 that "[p]roduction of the positive electrode active material of the present invention is conducted by firing a raw material mixture consisting of given proportions of salts and/or oxides of various element(s) and an addition element(s)], in an oxidizing atmosphere at 700-900 C for 5 to 50 hours." It is also important to note that the method in JP' 452 falls squarely within the conditions disclosed in the instant specification. Paragraph 107 of J'452 states that the raw materials were calcinated at 900 degrees C in the atmosphere, which is an oxidizing atmosphere for 10 hours.

The Examiner provided detailed reasons in the Grounds of Rejection as to why the methods of Zhong et al. ('104) are identical to applicant's disclosed method and would inherently yield the product having the claimed properties. Specifically, Zhong et al's ('104) formula in the Abstract encompasses those claimed by applicant as stated above. It is applicant's burden to provide experimental proof that the methods of Zhong et al. ('104) do not yield primary particles having substantially octahedral shape.

Applicant has not experimentally shown that the method of Zhong et al. do not produce primary particle having the claimed properties. Since the methods including the raw materials, temperature, and time to produce the lithium manganese oxides of Zhong et al. is similar, if not identical to applicant's disclosure, the methods produce positive

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active materials that would inherently encompass primary particles having the claimed properities.

Applicant argues that the Comparative Examples reported in the present specification are closer to the present invention than are the various disclosures in Zhong '104, thereby further disproving the notion of inherency (pg. 19).

The applicant has not specified in what ways the Comparative Examples reported in the present specification are closer to the present invention. If it is in terms of the closeness in the chemical compound, the Examiner disagrees and notes that the compound disclosed in Zong '104 (see Abstract) is much closer to the present invention than the Comparative Examples. If it is in terms of the process of making, the Examiner has fully addressed why Zhong '104 invention inherently encompasses the primary particles having the claimed proerties in the paragraph above.

Applicant argues that there is not motivation to combine Zhong '104 with Zhong '597 and Watanabe '975 (pg. 17).

The motivation has been clearly addressed in the Office Action mailed on 6/28/2005 and is reiterated in the Grounds of Rejection above.

Response to arguments to Issue 5, rejection of claims 11-14, 16-21, 23 under 35 USC 103(a), over Manev (US 5961949) in view of Zhong (US5700597) and Watanabe (US 6106975).

Applicant asserts that the conditions and formulas in the methods of Manev et al. ('104) are not identical to those of the present invention and would not produce primary particles having substantially octahedral shape and that the present specification at page 11, lines 5-10 do not inherently result in production of positive electrode active materials having the characteristics recited in the present claim (pg. 22).

In response, the applicant has not disproven the Examiner's inherency arguments of the Manev et al. ('949) reference because Manev states that $\text{Li}_{1.025}\text{Mn}_{1.975}\text{O}_4$ was prepared by mixing and firing at 750°C for 48 hours (6:1-10). Manev et al's ('949) formula in 6:1-10 encompasses those claimed by applicant. It is applicant's burden to provide experimental proof that the method of Manev et al. ('949) do not yield primary particles having substantially octahedral shape. Applicant has not experimentally shown that the method of Manev et al. do not produce primary particle having the claimed properties. Since the methods including the raw materials, temperature, and time to produce the lithium manganese oxides of Manev et al. is similar, if not identical to applicant's disclosure, the methods produce positive active materials that would inherently encompass primary particles having the claimed properities.

Applicant argues that the Comparative Examples reported in the present specification are closer to the present invention than are the various disclosures in Manev '949, thereby further disproving the notion of inherency (pg. 22).

The applicant has not specified in what ways the Comparative Examples reported in the present specification are closer to the present invention. If it is in terms of the closeness in the chemical compound, the Examiner disagrees and notes that the compound disclosed in Manev '949 (see 6:1-10) is much closer to the present invention than the Comparative Examples. If it is in terms of the process of making, the Examiner has fully addressed why Manev '949 invention inherently encompasses the primary particles having the claimed properties in the paragraph above.

Applicant argues that there is not motivation to combine Manev '949 with Zhong '597 and Watanabe '975 (pg. 23).

The motivation has been clearly addressed in the Office Action mailed on 6/28/2005 and is reiterated in the Grounds of Rejection above.

Response to arguments to Issue 6, rejection of claim 24 under 35 USC 103(a), over Zhong (US 5631104) in view of Zhong (US5700597) and Watanabe (US 6106975).

Applicant argues that no combination of Zhong '104, Zhong '597, Watanabe '975, and Idota '203 would render obvious any of the subject matter recited in claim 24.

The obviousness has been clearly addressed in the Office Action mailed on 6/28/2005 and is reiterated in the Grounds of Rejection above.

Response to arguments to Issue 7, rejection of claim 24 under 35 USC 103(a), over Manev (US 5961949) in view of Zhong (US5700597) and Watanabe (US 6106975).

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Applicant argues that no combination of Zhong '104, Zhong '597, Watanabe '975, and Idota '203 would render obvious any of the subject matter recited in claim 24.

The obviousness has been clearly addressed in the Office Action mailed on 6/28/2005 and is reiterated in the Grounds of Rejection above.

For the above reasons, it is believed that all the rejections should be sustained.

Respectfully Submitted,

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SUPERVISORY PATENT EXAMINER

Appendix A – Printout of <http://www.hyperdictionary.com>

Appendix B – Printout of <http://gallery.origami.free.fr>

Appendix C – English translation of JP 08-217452



English Dictionary Computer Dictionary Thesaurus Dream Dictionary Medical Dictionary

Search Dictionary:

Search

Meaning of REGULAR OCTAHEDRON

WordNet Dictionary

Definition: [n] an octahedron with eight equilateral triangles as faces

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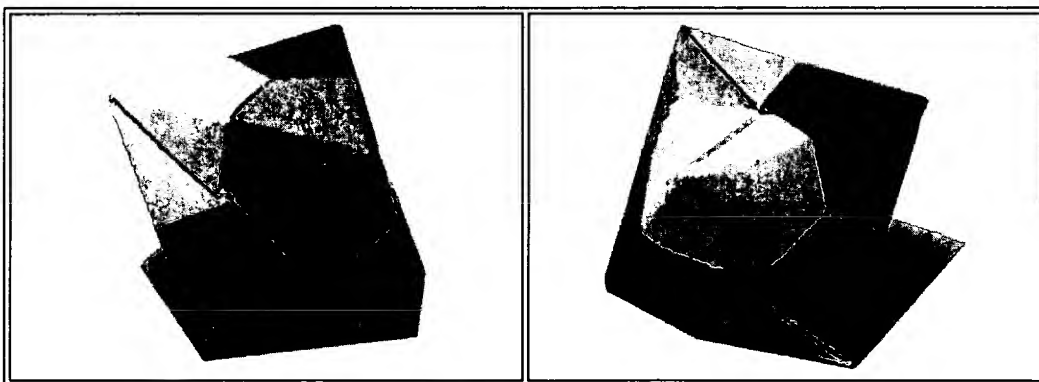
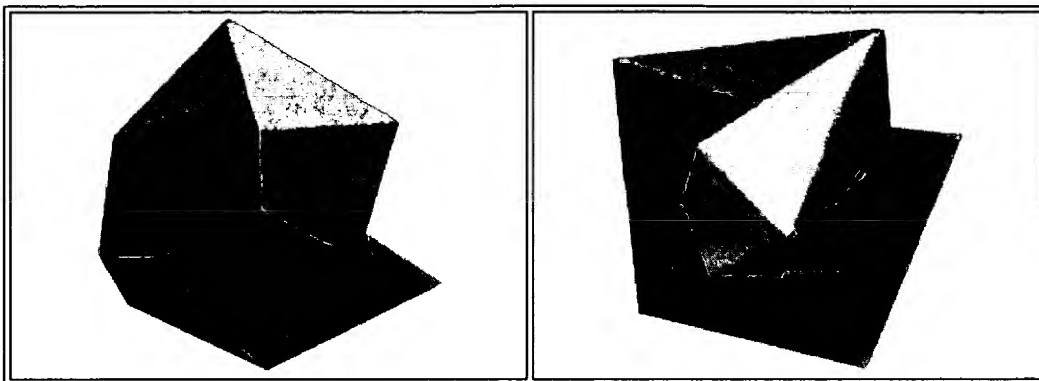
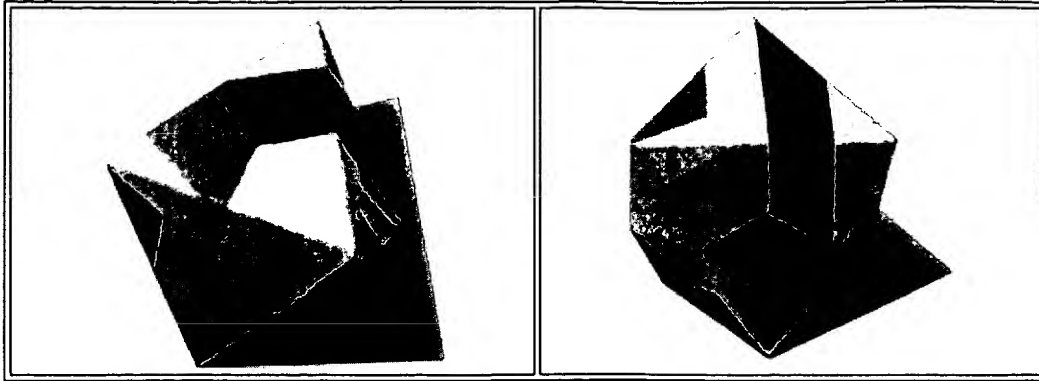
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See Also: ideal solid, Platonic body, Platonic solid, regular convex polyhedron, regular convex solid, regular po

Six-Fold Regular Octahedron



Creator : Tomoko Fuse
Folder : N. Terry
Photographer : N.Terry
Date : 2002

PTO 06-[2484]

Japanese Patent

Hei 8-217452

**MANGANESE COMPOSITE OXIDE, ITS MANUFACTURING METHOD,
AND ITS USAGE**

[Mangan Fukogo Sankabutsu Oyobi Sono Seizo Hoho
Narabini Sono Yoto]

Masaki Okada and Yoshio Yoshida

UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C.

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MANUFACTURING METHOD, AND ITS
USAGE

Specification

1. Title of the invention

Manganese Composite Oxide, Its Manufacturing Method, and
Its Usage

2. Claims

/2

1. A manganese composite oxide, characterized by the fact that in a manganese composite oxide, it is composed of particles with a particle diameter of 10 μm or less; the BET specific surface is 1 m^2/g or more; the crystal structure is a spinel type; and it is expressed by a chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M is at least one kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$).

2. The manganese composite oxide of Claim 1, characterized by the fact that the lattice parameter is smaller than 8.24 \AA .

3. A method for manufacturing the manganese composite oxide of Claim 1, characterized by the fact that a mixture of a manganese dioxide having a γ type crystal structure with a BET specific surface of 150-500 m^2/g , a lithium oxide, and at least

¹ Numbers in the margin indicate pagination in the foreign text.

one kind or more of metallic material being selected from Ni, Co, Fe, and Cr is sintered.

4. The method for manufacturing the manganese composite oxide of Claim 1, characterized by the fact that the lithium compound is lithium nitrate.

5. The method for manufacturing the manganese composite oxide of Claim 4, characterized by the fact that the metallic materials of Ni, Co, Fe, and Cr are their nitrates.

6. The method for manufacturing the manganese composite oxide of Claim 4, characterized by the fact that in the sintering in the method for manufacturing the manganese composite oxide of Claim 3, a second heat treatment at a temperature of 500-850°C is carried out after a first heat treatment at a temperature of 500°C or lower.

7. A lithium secondary battery, characterized by the fact that lithium, lithium alloy, or a compound which can occlude and discharge lithium is used as a negative electrode activator; a nonaqueous electrolyte is used as an electrolyte; and the manganese composite oxide of Claim 1 is used as a positive electrode activator.

3. Detailed explanation of the invention

[0001]

(Industrial application field)

The present invention pertains to a new manganese composite compound, its manufacturing method, and its usage.

Specifically, the present invention pertains to a manganese composite oxide that is composed of particles with a particle diameter of 10 μm or less, has a BET specific surface of 1 m^2/g or more, has a spinel type crystal structure, and is expressed by a chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M is at least one kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$), its manufacturing method, and a lithium secondary battery in which the manganese composite oxide is used in a positive electrode activator.

[0002] The manganese composite oxide is a material that has been most noticed among positive electrode activators for a lithium secondary battery since it is inexpensive, the raw material manganese is sufficient in terms of resource, and its synthesis is easy.

[0003] Since the lithium secondary battery can theoretically constitute a high-energy density battery, it has already been partially put into practice as a new secondary battery for the

next generation, and its research and development for high performances are actively advanced.

[0004]

(Prior art)

Along with the supply of cordless equipments of personal uses, the development of small-scale and lightweight lithium secondary batteries with a high energy density is strongly in demand.

[0005] Recently, the development of a lithium ion type secondary battery using a compound which can occlude and discharge lithium ions such as carbonaceous material and metal oxide without using lithium metal and lithium alloy as a negative electrode has been actively advanced.

[0006] For this reason, it is necessary to use a compound containing lithium as a positive electrode activator.

[0007] Currently, as the compound containing lithium, LiMO_2 type oxides (hereinafter, M is a transition metal) having a rock salt structure as a basic skeleton and having a layered structure in which lithium and transition metals are regularly arranged are attracted. Among them, since a lithium cobalt oxide (hereinafter, expressed by LiCoO_2) and a lithium nickel oxide (hereinafter, expressed by LiNiO_2) exhibit a battery voltage of

4V class, their research and development are actively advanced, including partial practical uses.

[0008] However, as problems being already indicated, the cobalt raw material is expensive in the LiCoO_2 , and the synthesis is difficult in the LiNiO_2 .

[0009] As materials showing the battery voltage of 4 V class other than the above-mentioned two materials, a lithium manganese spinel with a spinel type structure (hereinafter, expressed by LiMn_2O_4) is known.

[0010] Since LiMn_2O_4 is easily synthesized and the manganese raw material is sufficient in terms of resource and inexpensive, it is expected as a material for replacing LiCoO_2 and LiNiO_2 .

[0011] LiMn_2O_4 has a spinel structure and is a positive spinel type compound in which lithium is occupied at the spinel 8a site, manganese is occupied at 16d site, and oxygen is occulted at 32e site.

[0012] In other words, it has a structure in which 1/8 of the tetrahedron of a cubic close-packed oxygen is occupied by lithium and 1/2 of the octahedron position is occupied by manganese.

[0013] In case the LiMn_2O_4 is used in the positive electrode activator of the lithium secondary battery, an area functioning at a voltage of about 4 V and an area functioning at a voltage

of about 3 V are clarified. (Otsuki et al., 29th Battery Discussion Meeting Lecture Summary, P135, 1988).

[0014] In the area functioning at a voltage of about 4 V, lithium ions in the crystal lattice of LiMn_2O_4 move in the site occupied by lithium in the crystal structure via 16c site of a vacant oxygen octahedron position, and the incoming and outgoing reaction is advanced without destructing the structure in a state in which a cubic crystal of the original skeleton structure is maintained.

[0015] On the contrary, in an area functioning at a voltage of about 3 V, the incoming and outgoing reaction of lithium ions is advanced along with the change from a cubic crystal to a tetragonal crystal at 16 site of a vacant oxygen octahedron $\frac{1}{3}$ position in the crystal lattice of LiM_2O_4 .

[0016] Of the above-mentioned two reactions, in order to constitute a lithium secondary battery with a high energy density, it is important to utilize an area showing a voltage of about 4 V.

[0017] In case LiMn_2O_4 is made to function in the area showing a voltage of about 4 V, as mentioned above, since the charge and discharge reaction is advanced in a state in which the cubic crystal structure of the basic skeleton is maintained without a

change of the crystal system, many proposals of the application to the lithium secondary battery have been made up to now.

[0018] However, in the proposals up to now, the secondary battery with a high energy density could not be constituted, and its practical uses have not been realized yet.

[0019] In case LiM_2O_4 is made to function in the area showing a voltage of about 4 V, the charge and discharge reaction is advanced in a state in which the cubic crystal structure is maintained, the crystal lattice is expanded and contracted by the oxidation and reduction of manganese and the incoming and outgoing lithium ions, though it is slight.

[0020] According to the review of these inventors, in LiMn_2O_4 , the charge and discharge cycle, that is, the volume change due to the expansion and contraction of the crystal lattice is repeated, the collapse of a local crystal structure, the miniaturization of the particles, the electric conductivity decrease due to the miniaturization, and the electric conductivity decrease due to the contact inferiority with an electroconductive aid (for example, acetylene black, graphite, etc.) are caused, though it is slow. For this reason, the capacity is decreased along with the charge and discharge cycle.

[0021] Furthermore, in case the charge and discharge is carried out at a high charge and discharge rate, even if the charge

voltage is regulated so that LiMn_2O_4 is made to function in the area showing a voltage of about 4 V, the utilization of a positive electrode activator is made nonuniform by the decrease of the electric conductivity of a positive electrode by repeating the charge and discharge, so that the reduction is partially advanced up to the area showing a voltage of about 3 V and the crystal structure is transited. Thereby, the decrease of the above-mentioned electric conductivity is accelerated, and the reversibility is considerably lowered.

[0022] For the above reasons, it is decided that LiMn_2O_4 is still not practically used.

[0023] As a method for solving the above problems, a method that substitutes part of manganese by other elements is proposed.

[0024] For example, in Japanese Kokai Patent Application Nos. Hei 3[1991]-219571 and Hei 4[1992]-160769, $\text{Li}_x\text{M}_y\text{Mn}_{(2-y)}\text{O}_4$ ($0.85 \leq x \leq 1.15$, $0.02 \leq y \leq 0.5$) in which part of the manganese is substituted by at least one kind of Co, Cr, and Fe is proposed.

[0025] The purpose of these proposals is to prevent the fracture of the crystal structure, that is, the decrease of the discharge capacity by decreasing the lattice parameter and more strengthening the crystal structure through the substitution of part of the manganese by Co, Cr, and Fe.

[0026] However, the further strengthening of the crystal structure lowers the flexibility to the volume change of the crystal lattice due to the charge and discharge reaction, so that the decrease of the discharge capacity is still difficult to be prevented, though the degradation rate can be lowered.

[0027] Furthermore, in these proposals, the synthesis is carried out at 900°C, and since the compound particles being obtained at this temperature are large, if they are used in the positive electrode activator, the miniaturization of the particles due to the charge and discharge is easily advanced, so that the capacity is apt to be lowered.

[0028] On the other hand, in Japanese Kokai Patent Application No. Hei 5[1993]-36412, it is proposed that in $\text{LiA}_x\text{Mn}_{(2-x)}\text{O}_4$ (A is Fe and/or Cr, $0.1 \leq x \leq 0.4$) in which part of the manganese is substituted by at least one of Fe and Cr, Fe be heat-treated at a temperature of 650-800°C and Cr be heat-treated at a temperature of 650-850°C.

[0029] However, in this proposal, Mn_2O_3 is used as a manganese raw material. According to the review of these inventors, in case the synthesis is carried out at a temperature of 650°C or higher by using Mn_2O_3 , the particle diameter of the compound being obtained is large, and the miniaturization of the

particles due to the charge and discharge is easily advanced, so that the capacity is apt to be decreased.

[0030] As mentioned above, in the compound in which part of the manganese of LiMn_2O_4 is substituted by other elements, if it is used in the positive electrode activator of the lithium secondary battery, the cycle characteristic is insufficient, and this compound is not practically used at present.

[0031] On the other hand, along with the supply of cordless equipments of personal uses, the development of a small-scale and lightweight lithium secondary battery with a high energy density is strongly in demand.

[0032] Up to now, an ion type lithium secondary battery in which a carbonaceous material is used as a negative electrode and a nonaqueous electrolytic solution is used as an electrolyte has been put into practice, however in order to supply it broadly as a small-scale power source for public and an on-demand type power source for power storage, the development of a more inexpensive and more stable lithium secondary battery is in demand.

[0033]

(Problems to be solved by the invention)

The purpose of the present invention is to propose a new compound in which part of the manganese of LiMn_2O_4 is substituted

by other elements and its manufacturing method and to provide a manganese system lithium secondary battery with an excellent cycle characteristic in which this compound is used in a positive electrode activator.

[0034]

(Means to solve the problems)

These inventors earnestly reviewed the above-mentioned problems to solve them. As a result, a new manganese composite oxide, that is, a manganese composite oxide that was composed of particles with a particle diameter of 10 μm or less, had a BET specific surface of 1 m^2/g or more, had a spinel type crystal structure, and was expressed by a chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M was at least one kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$) for the first time. /4 Also, it was discovered that the manganese composite oxide could be synthesized by sintering a mixture of a manganese dioxide having a γ type crystal structure with a BET specific surface of 150-500 m^2/g , a lithium oxide, and at least one kind or more of metallic material being selected from Ni, Co, Fe, and Cr. Furthermore, it was discovered that when this manganese composite oxide was used in a positive electrode activator of a lithium secondary battery, a new manganese system lithium

secondary cell with an excellent cycle characteristic could be constituted. Then, the present invention was completed.

[0035]

(Operation)

Next, the present invention is explained in detail.

[0036] The manganese composite oxide of the present invention expressed by the chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M is at least one kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$) is a manganese composite oxide with a spinel structure in which 1/8 of the tetrahedron of the cubic close-packed oxygen is occupied by lithium and 1/2 of the octahedron position is occupied by at least one kind or more of metals being selected from Ni, Co, Fe, and Cr.

[0037] The manganese composite oxide of the present invention shows an X-ray diffraction pattern similar to LiMn_2O_4 in which the position of the diffraction peak is shifted to a high angle side. In other words, it is a manganese composite oxide in which the crystal lattice is smaller than LiMn_2O_4 .

[0038]

According to the review of these inventors, a manganese composite oxide in which the crystal lattice is smaller than LiMn_2O_4 is attained by the valence of a substitutional metal and the ion size.

[0039] In case part of the manganese is substituted by Ni, since the stable phase as an oxide of Ni is NiO, Ni is substituted as + 2 valences with part of the manganese, and + trivalent manganese is oxidized to + 4 valences in the compound, so that the crystal lattice is contracted.

[0040] In case the manganese is substituted by Co, since a stable phase as an oxide of Co is CoO or Co₃O₄, part of Co is substituted as + 2 valences or + 3 valences by part of the manganese. In case the manganese is substituted as + 2 valences, + trivalent manganese is oxidized to + 4 valences, and in case it is substituted as + 3 valences, the crystal lattice is contracted even in any case and both mixed types by the substitution effect by Co with an ion radius smaller than that of the manganese.

[0041] In case the manganese is substituted by Fe and Cr, since stable phases as oxides are respectively Fe₂O₃ and Cr₂O₃, they are substituted by part of the manganese as +3 valences. The crystal lattice is contracted by the substitution effect by Fe and Cr with an ion radius smaller than that of the manganese.

[0042] Owing to the above-mentioned effects, it is considered that the crystal lattice is smaller than LiMn₂O₄. Furthermore, from the above facts, the ratio of the contraction of the crystal lattice due to the amount being substituted depends on

the kind of metallic material being substituted and the amount being substituted.

[0043] Also, in addition to Ni, Co, Fe, and Cr, there are metals with an ion radius smaller than that of the manganese and metals with + 2 valences for forming stable oxides. However, if the ion radius is too small, it penetrates into the lithium site, and even + 2 valences, if the ion radius is too large, since the substitution reaction is caused, Ni, Co, Fe, and Cr being currently proposed are considered as the most excellent substitutional metals.

[0044] The manganese composite oxide of the present invention is a compound in which the crystal lattice is smaller than LiMn_2O_4 , and since the crystal lattice is small, the following effects are considered. The substitution of part of the manganese by at least one kind of Ni, Co, Fe, and Cr fundamentally reduces the amount of + trivalent manganese of the compound, and in functioning at a voltage of about 4 V, the amount of manganese related to the oxidation and reduction reaction is reduced. In other words, with the limitation of the amount of charge and discharge reaction, the amount of crystal lattice being expanded and contracted is reduced, so that the cycle characteristic is improved.

[0045] Furthermore, according to the review of these inventors, a compound in which the crystal structure is uniformly developed is attained by substituting part of the manganese by at least one of Ni, Co, Fe, and Cr. For this reason, even if the charge and discharge is carried out at a high charge and discharge rate, the charge and discharge reaction is uniformly advanced to the entire activator. If the discharge voltage is regulated so that it may be made to function in the area showing a voltage of about 4 V, the reduction reaction does not advance up to the area showing a voltage of about 3 V, and a reversible function is realized.

[0046] The size of the crystal lattice is preferably smaller than 8.24 Å. More specifically, the size is more preferably smaller than 8.24 Å and 8.10 Å or greater.

[0047] If the size of the crystal lattice is 8.24 Å or more, since the oxide is used in the positive electrode activator of the lithium secondary battery, the expansion and contraction of the crystal lattice due to the charge and discharge is increased, so that the collapse of the crystal structure is accelerated.

[0048] On the other hand, if the crystal lattice is smaller than 8.24 Å, the expansion and contraction of the crystal lattice due

to the charge and discharge is decreased, so that the cycle characteristic is improved.

[0049] If the crystal lattice is too small, since the diffusion in the solid phase of the lithium is in a difficult state, the crystal lattice is apt to be broken down along with the charge and discharge.

[0050] According to the review of these inventors, it was understood that if a high output type lithium secondary battery was constituted, 8.10 \AA or greater was preferable.

[0051] In substituting by at least one of Ni, Co, Fe, and Cr, as the amount being substituted, the value of x in the chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ is essentially 0.0-0.5, and more specifically, the value is preferably 0.05-0.2.

[0052] If the value of X is more than 0.5, as mentioned above, the crystal lattice of the compound being obtained is too small, and the synthesis of a spinel single-phase compound is difficult.

[0053] Also, in constituting a high-capacity lithium secondary battery, since it is necessary to make both the charge and discharge capacity and the cycle characteristic compatible, /5 the value of X is more preferably 0.05-0.2.

[0054] The manganese composite compound expressed by the chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M is at least one

kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$) of the present invention is essentially constituted by particles with a particle diameter of 10 μm or smaller.

[0055] Though its details are indistinct, since the particles have a particle diameter of 10 μm or smaller, if they are used in the positive electrode activator of the lithium secondary battery, the expansion and contraction of the crystal lattice due to the charge and discharge is easily absorbed between the particles, so that the decrease of the electric conductivity, which is considered due to the contact inferiority with an electroconductive aid, can be suppressed.

[0056] If the particle diameter is 10 μm or smaller, there is no particular limitation, however in consideration of the filling characteristic as a positive electrode activator, the filling characteristic as a positive electrode activator can be maintained by limiting the particle diameter to 1-10 μm , so that a high capacity type secondary battery can be constituted.

Thus, this range is preferable.

[0057] As the size of the surface area of the manganese composite oxide represented by the chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M is at least one kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$), the BET specific surface is essentially 1 m^2/g or more.

[0058] If the compound with a BET specific surface value of 1 m^2/g or more is used in the positive electrode activator of the lithium secondary battery, the contact of an electroconductive aid and an electrolytic solution is improved, and even if the charge and discharge is carried out at a high charge and discharge rate, the charge and discharge reaction is uniformly advanced to the entire activator, so that a high capacity type secondary battery with an excellent cycle characteristic can be constituted.

[0059] In consideration of the filling characteristic as a positive electrode activator, the filling characteristic as a positive electrode activator can be maintained by limiting the value of the BET specific surface to 10 m^2/g or less, so that a high capacity type secondary battery can be constituted. Thus, the value is especially preferably 5-10 m^2/g .

[0060] In the method for manufacturing the manganese composite oxide of the present invention, it is essential to use a manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m^2/g as a manganese source.

[0061] With the use of the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m^2/g as a manganese source, the reaction is uniformly advanced, the

particle growth is distinctly suppressed, and a manganese composite oxide with a uniform composition can be synthesized.

[0062] Though details of the mechanism of the reaction are not distinct, the following are considered. In the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m^2/g being used in the present invention, since its surface area is very large, the reactivity with the lithium compound is very high. Accordingly, the manganese composite composition with a uniform composition is easily generated.

[0063] Also, since the manganese dioxide having a γ type crystal structure has a channel structure of (1 x 2) and the diffusion path of lithium in the crystal is secured, if it is reacted with a lithium compound, the reaction is easily advanced.

Furthermore, since the surface area is very large, the composite formation with a metallic material is also easily advanced, so that a manganese composite oxide with a uniform composition is easily generated, though the reason is indistinct.

[0064] This effect is distinct when the BET specific surface is 150-500 m^2/g . It is considered based on the following reasons.

[0065] If the BET specific surface is more than 500 m^2/g , a thermal phase transition of the manganese dioxide is more easily caused than the composite formation reaction of the lithium

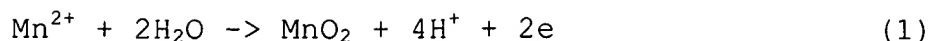
compound and the metallic material, so that the channel structure in which lithium is easily diffused (1 x 2) is distorted, the composite formation reaction is difficult to be advanced, so that the manganese composite oxide with a uniform composition is difficult to be manufactured and the aggregation of the particles is apt to be caused. Thereby, a manganese composite oxide of 10 μm or smaller cannot be manufactured.

[0067] For the above-mentioned reasons, it is considered that if the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m^2/g is used as a manganese source, a manganese composite oxide with a uniform composition can be easily manufactured.

[0068] The manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m^2/g being used in the present invention, for example, as shown in Japanese Kokoku Patent No. Sho 41[1966]-1696, can be manufactured by an electrolysis reaction at a high sulfuric acid concentration and a high current density, compared with the ordinary manufacture conditions of an electrolytic manganese dioxide.

[0069] Under the ordinary manufacture conditions, the electrolytic manganese dioxide is precipitated in an anode shape by the oxidation reaction shown in the equation (1).

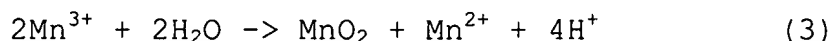
[0070]



For this reason, after finishing the electrolysis, peeling-off is carried out from the anode, and a crushing treatment is applied, so that a particle-shaped manganese dioxide is formed. The BET specific surface of the manganese dioxide being obtained by this method is 100 m²/g or less.

[0071] On the other hand, the manganese dioxide with a γ type crystal structure being used in the present invention is manufactured by increasing the stability of Mn^{3+} ions by raising the sulfuric acid concentration in the electrolytic solution, compared with the ordinary manufacture conditions of an electric manganese dioxide, forming only Mn^{3+} ions as an anode product as shown in the equation (2), and applying a hydrolysis reaction shown by the equation (3) in an electrolytic solution.

[0072] /6



In the above-mentioned method, the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m²/g can be manufactured.

[0073] As the lithium material being used in the manufacture of the manganese composite oxide of the present invention, any of lithium and/or lithium compounds may be used. For example,

lithium metal, lithium hydroxide, lithium oxide, lithium carbonate, lithium iodide, lithium nitrate, lithium oxalate, alkyl lithium, etc., are mentioned, however lithium materials being melted at a temperature of 500°C or lower are preferable. Among them, lithium nitrate is more preferable.

[0074] As the metallic material being used in the manufacture of the manganese composite oxide of the present invention, any of metals and/or metal oxides may be used. For example, metal, metal hydroxide, metal oxide, metal carbonate, metal nitrate, organometal complex, etc., are mentioned, and metallic materials being melted at 500°C or lower are preferable. Among them, a metal nitrate is more preferable.

[0075] The method for mixing the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m²/g, the lithium compound, and at least one kind or more of metallic material being selected from Ni, Co, Fe, and Cr is not particularly limited, and the mixture in a solid phase and/or a liquid phase may be employed. For example, a method that mixes the powder of the above-mentioned raw materials by a dry type and/or a wet type and a method that adds the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m²/g into a solution in which the lithium compound and the metallic material are dissolved and/or suspended and mixes

them by stirring are mentioned. The method for sintering the manganese composite oxide that sinters the mixture of the manganese dioxide with a γ type crystal structure having a BET specific surface of 150-500 m^2/g , the lithium compound, and at least one kind or more of metallic material being selected from Ni, Co, Fe, and Cr is not particularly limited, however as a preferable sintering, after applying the first heat treatment at a temperature of 500°C or lower in an air and/or oxygen, the second heat treatment may be carried out at a temperature of higher than 500°C and 850°C or lower.

[0076] According to the review of the present invention, around 500°C as a boundary, the composite formation reaction is advanced at a lower temperature side, and a spinel structure is developed at a higher temperature side. Therefore, the composite formation reaction is sufficiently advanced in the first heat treatment, and the crystal growth reaction is carried out in the second heat treatment, so that a manganese composite oxide in which the composition is more uniform and the spinel structure is developed can be synthesized. Furthermore, the composite formation reaction is further accelerated by applying the first heat treatment in an air and/or oxygen.

[0077] Also, if the second heat treatment is applied at a temperature higher than 850°C, since the particle growth and the

reduction reaction of manganese are easily caused, 850°C or lower is preferable.

[0078] Also, the baking time is not particularly limited, however 10 h or more is preferable in both the first heat treatment and the second heat treatment.

[0079] As the negative electrode of the lithium secondary battery of the present invention, lithium metal, lithium alloys, or compounds which can occlude and discharge lithium can be used, and as the lithium alloys, for example, lithium/tin alloy, lithium/aluminum alloy, lithium/lead alloy, etc., are mentioned. Also, as the compounds that can occlude and discharge lithium, oxides, carbonaceous materials such as graphite, iron oxides such as FeO, Fe₂O₃, and Fe₃O₄, cobalt oxides such as CoO, CoO₃, and Co₃O₄, etc., are mentioned.

[0080] Also, the electrolyte of the lithium secondary battery of the present invention is not particularly limited, and for example, an electrolyte in which at least one kind or more of lithium salts such as lithium perchlorate, lithium tetrafluoroborate, lithium hexafluorophosphate, and lithium trifluoromethanesulfonate or inorganic, organic lithium ion-electroconductive solid electrolytes, etc., can be used. Using the positive electrode activator of the manganese composite

oxide obtained in the present invention, a battery shown in Figure 1 was constituted.

[0081] In the figure, 1 is a lead wire for a positive electrode, 2 is a mesh for a current collection of the positive electrode, 3 is a positive electrode, 4 is a separator, 5 is a negative electrode, 6 is a mesh for a current collection of the negative electrode, 7 is a lead wire for the negative electrode, and 8 is a case.

[0082] Next, application examples are shown as detailed examples of the present invention, however the present invention is not limited to these application examples.

[0083]

(Application examples)

Also, the X-ray diffraction measurement, the particle structure observation, the specific surface measurement in the application examples of the present invention and a comparative example were carried out by the following methods.

[0084]

X-ray diffraction measurement:

Measurer: MXP3 made by Max Science Co.

Irradiating X-rays: Cu K α rays

Measurement mode: Step scan

Scan condition: 0.04° as 2 θ

Measurement time: 5 sec

Measurement range: 10-70° as 2θ

/7

Observation of particle structure:

Measurer: Scanning electron microscope

JEOL Ltd.

Acceleration voltage: 15 KV

Surface area measurement:

Measurer: BET method specific surface measurer

Measuring method: It was measured by an automatic surface area measurer (ASA-2000 made by Shimata Scientific Equipment Industry K.K.) after treating at 250°C for 40 min in a nitrogen gas flow (flow velocity: 15 mL per min).

[0085] Also, the length of the crystal axis was determined from X-ray diffraction measurement data of each compound by a WPPD method (Whole-Powder-Pattern Decomposition Method).

[0086] Furthermore, the composition analysis was measured by an ICP emission analysis method.

[0087] <Manufacture of manganese composite oxide>

Application Example 1: Manufacture of $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$

As Application Example 1, $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$ was manufactured by the following method. A particle-shaped electrolytic manganese dioxide was obtained by electrolyzing at a current density of 50 A/dm², using a Pt plate as an anode, in an aqueous solution

containing manganese sulfate at 25 g/L and sulfuric acid at a concentration of 150 g/L. As a result of the analysis of the electrolytic manganese dioxide, it was a manganese dioxide with a γ type crystal structure having a BET specific surface of 150-190 m²/g and a particle diameter of 1 μ m or smaller.

[0088] Next, the manganese dioxide, lithium nitrate (special-grade reagent), and cobalt nitrate hexahydrate (special-grade reagent) were mixed at a mole ratio of Li:Mn:Co = 1:1.9:0.1 and sintered at a temperature of 450°C for 24 h in the air.

[0089] Next, it was cooled down to room temperature, crushed in a mortar, mixed, and sintered at a temperature of 650°C for 24 h in the air.

[0090] The X-ray diffraction pattern of the compound obtained is shown in Figure 2, and the particle structure observation result is shown in Figure 3. As a result of the chemical analysis, the measurement results of the length of the crystal axis and the BET specific surface were shown in Table I.

[0091]

(Table I)

// Insert Table I //

	化学組成	a 軸の長さ (Å)	BET 比表面積 (m ² /g)	容量維持率 (%)
実施例 1	LiCo _{0.9} Mn _{0.1} O ₂	8.227	8.5	95
実施例 2	LiCo _{0.9} Mn _{0.1} O ₂	8.219	9.0	98
実施例 3	LiNi _{0.9} Mn _{0.1} O ₂	8.235	8.3	96
実施例 4	LiFe _{0.9} Mn _{0.1} O ₂	8.238	7.8	95
実施例 5	LiCr _{0.9} Mn _{0.1} O ₂	8.237	8.2	96
比較例 1	LiCo _{0.9} Mn _{0.1} O ₂	8.222	0.6	90

1. Chemical composition
2. Length of a-axis (Å)
3. BET specific surface (m²/g)
4. Capacity retention rate (%)
5. Application Example 1
6. Application Example 2
7. Application Example 3
8. Application Example 4
9. Application Example 5
10. Comparative Example 1

[0092] As a result of the analysis, it was understood that the compound obtained was a manganese composite oxide composed of particles of 5 μm or smaller with a spinel structure represented by $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$ having a crystal axis length of 8.227 Å and a BET specific surface of 8.5 m^2/g .

[0093] Application Example 2: Manufacture of $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$

As Application Example 2, the manufacture was carried out similarly to Application Example 1 except for mixing Li, Mn, and Co at a mole ratio of 1:1.8:0.2.

[0094] As a result of the analysis, the compound obtained was a manganese composite oxide composed of particles of 5 μm or smaller with a spinel structure.

[0095] As a result of the chemical analysis, the measurement results of the length of the crystal axis and the BET specific surface were shown in Table I.

[0096] Application Example 3: Manufacture of $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$ /8

As Application Example 3, $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$ was manufactured by the following method. The manganese dioxide manufactured in Application Example 1, lithium nitrate (special-grade reagent), and nickel nitrate hexahydrate (special-grade reagent) were mixed at a mole ratio of $\text{Li}:\text{Mn}:\text{Ni} = 1:1.9:0.1$ and sintered at a temperature of 450°C for 24 h in the air.

[0097] Next, it was cooled down to room temperature, crushed in a mortar, mixed, and sintered at a temperature of 650°C for 24 h in the air.

[0098] As a result of the analysis, it was understood that the compound obtained was a manganese composite oxide composed of particles of 5 μm with a spinel structure represented by $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$ having a crystal axis length of 8.235 Å and a BET specific surface of 8.3 m^2/g . As a result of the chemical analysis, the measurement results of the length of the crystal axis and the BET specific surface were shown in Table I.

[0099] Application Example 4: Manufacture of $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$

As Application Example 4, $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$ was manufactured by the following method. The manganese dioxide manufactured in Application Example 1, lithium nitrate (special-grade reagent), and iron nitrate nanohydrate (special-grade reagent) were mixed at a mole ratio of $\text{Li}:\text{Mn}:\text{Fe} = 1:1.9:0.1$ and sintered at a temperature of 450°C for 24 h in the air.

[0100] Next, it was cooled down to room temperature, crushed in a mortar, mixed, and sintered at a temperature of 850°C for 24 h in the air.

[0101] As a result of the analysis, it was understood that the compound obtained was a manganese composite oxide composed of particles of 10 μm or smaller with a spinel structure

represented by $\text{LiF}_{0.1}\text{Mn}_{1.9}\text{O}_4$ having a crystal axis length of 8.238 Å and a BET specific surface of 7.8 m²/g.

[0102] As a result of the chemical analysis, the measurement results of the length of the crystal axis and the BET specific surface were shown in Table I.

[0103] Application Example 5: Manufacture of $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$

As Application Example 5, $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$ was manufactured by the following method. The manganese dioxide manufactured in Application Example 1, lithium nitrate (special-grade reagent), and chromium nitrate nanohydrate (special-grade reagent) were mixed at a mole ratio of Li:Mn:Cr = 1:1.8:0.2 and sintered at a temperature of 450°C for 24 h in the air.

[0104] Next, it was cooled down to room temperature, crushed in a mortar, mixed, and sintered at a temperature of 850°C for 24 h in the air.

[0105] As a result of the analysis, it was understood that the compound obtained was a manganese composite oxide composed of particles of 10 μm or smaller with a spinel structure represented by $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$ having a crystal axis length of 8.237 Å and a BET specific surface of 8.2 m²/g.

[0106] As a result of the chemical analysis, the measurement results of the length of the crystal axis and the BET specific surface were shown in Table I.

[0107] Comparative Example 1: Manufacture of $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$

As Comparative Example 1, $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$ was manufactured by the following method. Lithium carbonate (special-grade reagent), Mn_3O_4 (trimanganese tetraoxide), and basic cobalt carbonate (special-grade reagent) were mixed at a mole ratio of $\text{Li}:\text{Mn}:\text{Co} = 1:1.8:0.2$ and sintered at a temperature of 900°C for 10 h in the air. The X-ray diffraction pattern of the compound obtained was shown in Figure 2, and the particle structure observation result was shown in Figure 4. As a result of the chemical analysis, the measurement results of the length of the crystal axis and the BET specific surface were shown in Table I. As a result of the analysis, it was understood that the compound obtained was a manganese composite oxide composed of acicular regular octahedron particles with a one side length of $1\ \mu\text{m}$ or greater having a spinel structure represented by $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_{3.8}$ having a crystal axis length of $8.222\ \text{\AA}$, however its BET specific surface was $0.6\ \text{m}^2/\text{g}$.

[0108] <Constitution of battery> The manganese composite oxides manufactured in Application Examples 1-5 and Comparative Example 1 were mixed with a mixture of polytetrafluoroethylene and acetylene black as an electroconductive aid (trade name: TAB-2) at a weight ratio of 2:1. 75 mg of the mixture was molded at a

pressure of 1 ton/cm² into a pellet shape on a mesh of 20 mmØ (SUS 316) and dried at 200°C for 5 h under reduced pressure.

[0109] Using it as the positive electrode 3 of Figure 1 and a lithium segment cut out of a lithium foil (0.2 mm in thickness) as the negative electrode 5 of Figure 1, an electrolytic solution in which lithium perchlorate was dissolved at a concentration of 1 mol/dm³ in propylene carbonate was impregnated in the separator 4 of Figure 1, so that a battery shown in Figure 1 with a sectional area of 2.5 cm² was constituted.

[0110] <Evaluation of battery performances> Using the battery prepared in the above-mentioned method, its charge and discharge were repeated at a fixed current of 1.0 mA/cm² and a battery voltage of 4.5-3.5 V.

[0111] The ration of the discharge capacity at 50 cycles to the discharge capacity at 1 cycle, that is, the capacity retention rate was shown in Table I.

[0112] The manganese composite oxides manufactured in Application Examples 1-5 showed a high retention rate of 95% or more, however the manganese composite oxide manufactured in Comparative Example 1 was 90%. The results are shown in Table I.

[0113]

(Effects of the invention)

As mentioned above, the manganese composite oxide of the present invention is a new manganese composite oxide that is composed of particles with a particle diameter of 10 μm or smaller, has a BET specific surface of 1 m^2/g or more, has a spinel type crystal structure, and is represented by a chemical formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ (in the formula, M is at least one kind or more being selected from Ni, Co, Fe, and F, and $0.0 < x \leq 0.5$). If this new manganese composite oxide is used in a positive electrode, a new manganese system lithium secondary battery /9 with an excellent cycle characteristic can be constituted.

[0114] The discovery of the manganese system positive electrode material applicable to a positive electrode activator of a lithium secondary battery is an industrially useful knowledge.

4. Brief description of the figures

Figure 1 is a cross section showing an embodiment of a battery constituted in application examples and a comparative example.

Explanation of numerals:

- 1 Positive electrode lead wire
- 2 Mesh for a current collection of the positive electrode
3. Positive electrode
- 4 Separator

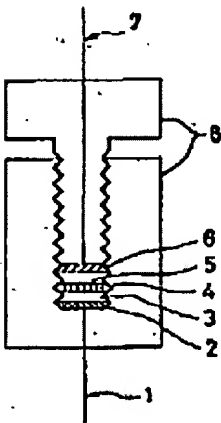
- 5 Negative electrode
- 6 Mesh for a current collection of the negative electrode
- 7 Lead wire for the negative electrode
- 8 Case

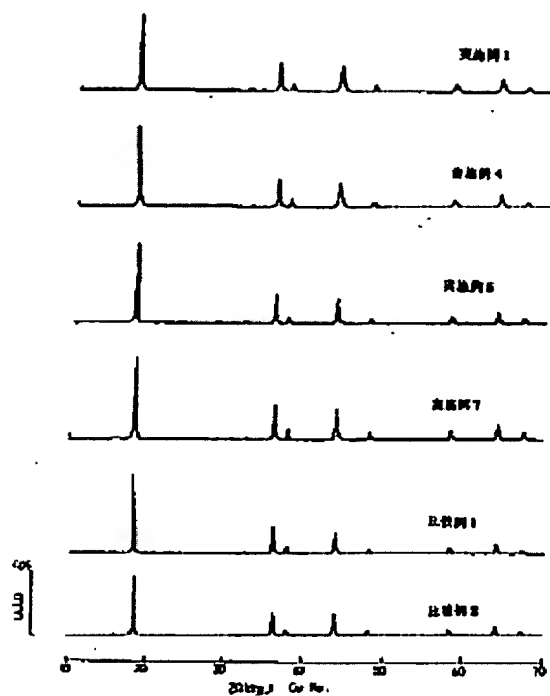
Figure 2 is an X-ray diffraction diagram showing the manganese composite oxides manufactured in Application Example 1 and Comparative Example 1

Figure 3 is a photo showing the particle structure of the manganese composite oxide manufactured in Application Example 1.

Figure 4 is a photo showing the particle structure of the manganese composite oxide manufactured in Comparative Example 1.

Figure 2:





1. Application Example 1
2. Application Example 4
3. Application Example 6
4. Application Example 7
5. Comparative Example 1
6. Comparative Example 2

Figure 3:

1. Photo

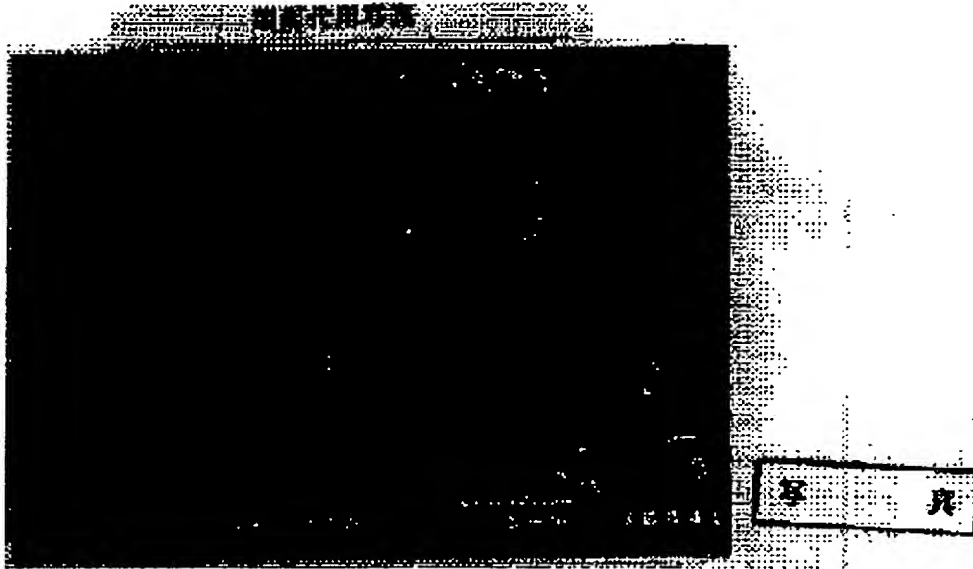


Figure 4:

1. Photo

